

Application performance of three common solid-state electrolytes in batteries

Yanyi Liu^{1, *}, Haoxuan Peng² and Liqing Zhang³

¹College of Materials Science and Engineering, Xi'an University of Architecture and Technology, Xi'an, China

²School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan, China

³Queen Mary College of Engineering, Northwestern Polytechnical University, Xi'an, China

* Corresponding Author Email: liuyanyi@xauat.edu.cn

Abstract. Due to the hidden benefits such as the possibilities to make energy density high, safety improved, and lifespan extended, solid-state batteries are a focal point in battery technology research. Current liquid electrolyte-based lithium-ion batteries, despite their maturity, have inherent issues like safety risks and limited energy density. While the advancement in solid-state battery technology can potentially overcome certain challenges, it also encounters its own issues including high contact interface impedance and ion transmission efficiency. For solid-state batteries to supplant traditional lithium-ion batteries in the future, these challenges must be addressed. The research provides an in-depth analysis of the three major types of solid-state electrolytes currently prevalent in the market, including oxide, sulfide, and polymer electrolytes. This is especially true for the electrochemical analysis of batteries after the electrolyte has been used. Each has its unique properties, synthesis methods, and limitations. Oxide electrolytes excel in high-temperature ionic conductivity but underperform at room temperature. Moreover, the synthesis of oxide solid electrolytes requires fine control over temperature and atmosphere, thus demanding high technical expertise. The sulfide category shows promise in room temperature conductivity, albeit with stability issues. Polymer electrolytes, however, are flexible and processable but have generally lower ionic conductivity. To enable large-scale applications, future research needs to focus on improving these electrolytes' performance and developing cost-effective and efficient synthesis methods. The importance of research into solid-state lithium-ion batteries is tied to their capacity to transform the energy storage sector.

Keywords: solid-state batteries, electrolytes, application.

1. Introduction

With the rapid growth of population and the development of science and technology, the world's energy demand is increasing year by year. By 2030, more than 80% of human energy will still come from fossil fuels, which will bring problems such as carbon emissions and energy depletion [1]. Therefore, the generation of sustainable energy, such wind and solar power, has emerged as a key area for research. During the past few years, there has been a notable increase in the generation of renewable energy. However, the solar radiation and the intensity of wind varies with the weather and time, resulting in a mismatch between energy supply and demand. Batteries and other energy storage devices can increase the control and predictability of renewable energy output. Solar energy or wind energy is converted into electrical energy by generators, and batteries then convert the electrical power obtained from the generating equipment into chemical energy for storage. The application of batteries can energy utilization efficiency, such as the storage of solar energy produced during daylight hours for subsequent use during nighttime.

In the realm of batteries, the traditional electrolyte serves as a conduit for ionic conduction, facilitating the seamless movement of ions between the positive and negative electrodes. Typically, traditional electrolytes are encountered in solution form, where compounds dissolve into ions, establishing an environment conducive to ion transport. An electrolyte can be defined as a substance

possessing remarkable ionic conductive properties, capable of disintegrating into charged ions when dissolved in a solution or in a molten state.

Traditional electrolytes used in lithium-ion batteries possess favorable ion conductivity and reactivity. They commonly consist of organic solvents with lithium salts like lithium hexafluorophosphate or ethylene carbonate. These electrolytes are extensively used in numerous sectors, such as energy storage structures. Traditional electrolytes offer excellent ion transport and benefit from well-established technologies and processes. Nevertheless, they suffer from safety risks, limited battery lifespan, and environmental impacts.

To overcome these limitations, researchers are actively exploring new electrolyte materials like solid-state electrolytic substances and electrolytic polymers [2]. To address the safety risks, limited battery lifespan, and environmental impacts associated with traditional electrolytes utilized in lithium-ion energy cells, researchers are actively exploring advanced electrolyte materials. One promising avenue of research is the advancement in solid-state battery technology.

Solid-state battery possesses several key advantages over their liquid electrolyte counterparts such as being non-combustible, non-corrosive, non-volatile, and resistant to high temperatures. The current solid-state battery is mainly categorized into two based on the electrolyte material: organic and inorganic systems. Inorganic systems are divided into oxide, sulfide, and halide systems, while organic electrolytes mainly use polyethylene oxide (PEO).

Polymers present a significant challenge, as their ionic conductivity is low and their electrochemical window is narrow. Due to these limitations, their upper-performance limit is also low [3]. The primary disadvantages of the oxide material system are its low overall conductivity and inadequate electrode connectivity, both of which may now be further enhanced through structure and preparation processes. The contact between the sulfides and the positive and negative electrodes is suboptimal. To overcome this problem, a bilayer electrolyte has been developed which uses different modification processes on either side of the interface to achieve better electrode contact. Sulfide increases the complexity of the preparation process and adds significant cost to large-scale production, as it readily reacts with water and oxygen present in the atmosphere to form toxic gases. Although the industry is still debating the possibility of commercializing solid-state batteries, further improvements in energy density, power density, circulation life, and safety are still the focus of solid-state battery development research, and research into low-cost, high-performance electrodes and solid-state electrolyte materials will be a vital factor in achieving this goal. Due to the excellent electrochemical performance of solid-state electrolytes, this research will mainly analyze the application performance of three common solid-state electrolytes in solid-state batteries, including sulfide solid-state electrolyte, solid polymer electrolytes and oxide solid electrolytes.

2. Application of different electrolytes in solid-state batteries

2.1. Sulfide solid-state electrolyte

Comparable Li^+ conduction to that of liquid electrolytes is crucial for the commercial viability of ASSLIBs, as evinced by sulfide solid-state electrolytes (SSEs). The sulfide SSE is a derivative of the oxide SSE, where S atoms replace O atoms. As a consequence, sulfide SSE has a wider Li^+ transport channel than oxide SSE, even though they have identical crystal structures. Moreover, S^{2-} binds to Li less strongly than O^{2-} . Consequently, more Li^+ ions are transported in sulfide SSE, resulting in higher ionic conductivity than oxide SSEs [4].

Although the conductivity rates of SSEs are comparable to those of liquid electrolytes, their electrochemical window is too narrow, resulting in significant contact losses at the interface during cycling. As a result, the potential applications of sulfide all-solid-state lithium batteries are greatly limited. However, according to Zhou's report, the use of 5,7,12,14-pentaphenyltetrone in the production of ASSLIB using a vulcanization electrolyte made from glass-ceramic $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$ (LPS) solves this problem [5]. Several in situ analyses have indicated that the decomposition of LPS can be considered negligible and that any impedance on the interface can be reversed through the

optimization of carbon additives. And the prepared solid-state battery has an excellent recyclability, as shown in Fig. 1. High specific capacity and excellent capacity retention achieved by PT-based ASSLBs surpassing previous reports [6], because of the low Young's moderate of PT electrodes, interfacial contact loss can be effectively prevented. Additionally, an ASSLB was created by incorporating Mo_6S_8 as a conductive additive in the platinum-based cathode, which exhibited better rate performance and longer life.

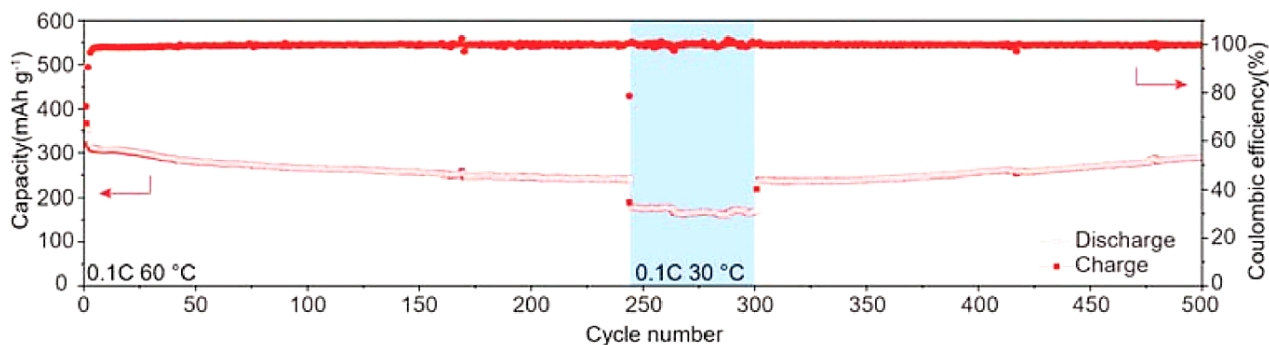


Fig. 1 The recyclability of the prepared solid-state battery [5].

Furthermore, the chemical instability of sulfide SE in the atmosphere and its electrochemical inconsistency with the electrode materials, namely lithium metal anode and oxide cathode, severely hinder the commercial application of sulfide SE. In order to overcome this challenge, Li et al. prepared the sulfide-doped composite electrolyte (SCE) by combining inorganic sulfide lithium arawite (Li_7PS_6) with polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) polymer [7]. Li_7PS_6 is embedded within the PVDF-HFP polymer matrix, resulting in an air-stable and flexible SCE with exceptional chemical and electrochemical stability. By using SCEs in which the presence of sulfide facilitates the movement of lithium ions, lithium-ion symmetric batteries can achieve up to 1,000 hours of continuous cycling at low current densities, thereby maintaining high conductivity and improving stability. Hexasulfide thiuram has been identified as a cost-effective sulfide electrolyte-based cathode material for solid-state organic batteries. Significantly, it shows a capacity of 600 mA h g^{-1} and can retain up to 80.8% of its capacity after 500 cycles. However, during cycling, there were oscillatory stress changes measuring up to 0.6 MPa, predominantly on the anode side. It has a very high energy density of 1140 Wh/kg , representing one of the highest performing organic cathodes reported to date [8].

2.2. Solid polymer electrolytes

Solid polymer electrolytes (SPEs), which are also referred to as dry solid polymer electrolytes, consist of a polymer matrix in conjunction with a lithium salt acting as a solute. The lithium salt facilitates ion conductivity. Compared to liquid electrolytes and solid inorganic electrolytes, solid polymer electrolytes have better adaptability to electrodes because they are less affected by electrode volume changes during charging and discharging processes and have better electrode compatibility. Additionally, they have good processability and lower flammability.

LLZO, a garnet-type oxide electrolyte, is specifically mentioned for its high stability and conductivity, and it has excellent stability when in contact with Li metal. PEO has better adaptability to electrodes and lower flammability compared to liquid electrolytes and solid inorganic electrolytes. The interface between polymer electrolytes and electrodes is identified as a key factor affecting battery performance, and strategies to improve the interface contact are mentioned. Sulfide solid-state electrolytes are being investigated as a potential electrolyte, however, challenges arise due to their restricted electrochemical range and the occurrence of contact losses at the interface. The article presents recent research on overcoming these challenges, such as using an organoquinone cathode and optimizing carbon additives. The article investigates the utilization of solid electrolytes, emphasizing that in order to successfully commercialize all-solid-state lithium-ion batteries.

A PEO stands out among SPEs as the most extensively utilized polymer matrix, owing to its robust capability to dissolve lithium salts and exhibit commendable electrochemical stability. Within PEO-based SPEs, ion conduction primarily takes place in the amorphous segment of the PEO matrix, with restricted ion movement in the crystalline region. Consequently, the ion conductivity of PEO-based SPEs is predominantly contingent upon the properties of the polymer matrix, encompassing its lithium salt solvation capacity and the proportion of crystalline to amorphous phases. Nevertheless, PEO-based SPEs typically manifest low ion conductivity, posing constraints on their broader applicability. To surmount this challenge, various modification strategies have been implemented, encompassing the integration of inorganic materials into the polymer matrix, adjustment of lithium salt ratios, and structural modifications to the matrix.

In addition to the ion conductivity of polymer electrolytes, the interface between polymer electrolytes and electrodes plays a crucial role in determining battery performance. Insufficient contact area between the cathode and the electrolyte necessitates achieving a sufficient and tight interface contact [9]. For example, one strategy to enhance this interface issue is the utilization of multilayer polymer electrolytes, such as employing a polymer matrix with high oxidation resistance at the cathode/electrolyte interface.

2.3. Oxide solid electrolytes

Oxide solid electrolytes belong to a class of materials renowned for their exceptional fast ion conduction properties. Within this category, oxide electrolytes of perovskite-type, NASICON-type, and those of the garnet-type have shown remarkable overall ionic conductivities exceeding 1 or potentially even 10 mS/cm, characterized by relatively low activation energies ranging from 0.2 to 0.3 eV. However, when it comes to lithium-conducting oxides, only a select few have exhibited ion conductivities surpassing the 1 mS/cm threshold [10]. Significant instances in this context encompass LLTO, LATP, LLZO, and the newly identified LiTa_2PO_8 .

Amongst these substances, LLZO is distinct because of its capacity to attain an overall conductivity that exceeds 1 mS/cm and its exceptional stability when interacting with Li metal—a crucial factor for its practical use [11]. Conversely, other lithium-conducting oxides face limitations such as substantial resistance at the interfaces of grains or lack of stability when paired with Li-metal anodes. For instance, LLZO, the garnet-structured oxide electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, displays exceptional features that position it as one of the most potential lithium-ion conductive oxides. It offers rapid Li-ion conductivity, elevated stability in the presence of Li metal, and a broad electrochemical window. The unaltered LLZO phase can exist in two polymorphic forms: tetragonal and cubic [11]. The tetragonal phase, which remains stable up to temperatures of 100-150 °C, shows low ionic conductivity under ambient conditions of approximately 10^{-7} S/cm. In contrast, the higher-temperature stable cubic phase displays significantly higher ionic conductance, varying between 10^{-4} to 10^{-3} S/cm.

3. Conclusion

In order to develop an ideal solid-state lithium battery, it is imperative to have outstanding mechanical and electrochemical properties. This article examines the performance of three different categories of newer solid electrolytes: oxidic, sulphidic, and polymeric. If we consider solely the electrolyte's performance, these three types of SSEs have made remarkable strides in recent years. The electrochemical properties of ASSLB, such as its ionic conductivity, electrochemical stability, and lithium-ion transfer quantity, mostly meet the requirements for practical applications. Consequently, commercialization appears to be on the horizon. Nevertheless, when evaluating its application in solid-state batteries, we can see that significant advances are still needed.

In the majority of reported studies, organic polymer materials such as PEO and polymers with similar structures have been chosen for the electrolytes of solid-state lithium batteries. However, poly(ethylene oxide) solid electrolytes containing lithium salts exhibit inadequate high-voltage

resistance to the positive electrode, and oxidation of ternary materials takes place at conventional voltages, hence restricting cathode material choice and greatly reducing the energy density. Furthermore, the durability of poly(ethylene oxide) is relatively low, and its resistance to puncture short circuits is weaker than that of alternative solid electrolyte systems.

The electrode-electrolyte interface contact ability and interfacial stability during cycling are poor for oxide solid electrolytes, resulting in a rapid increase in interfacial impedance during cycling. This leads to insufficient effective capacity of the negative electrode and faster decay of battery life, with difficulty even in thin layers. Therefore, oxide solid electrolytes frequently necessitate the inclusion of polymer components and mixtures with trace ionic liquids or high-performance lithium salt electrolytes, or the implementation of assisted in-situ polymerization to produce quasi-solid-state batteries that retain some safety advantages and enhance the electrolyte-electrode interfacial connection. Despite extensive ongoing research to improve interfacial contact capability, there is still significant progress to be made.

When utilizing sulfide solid electrolytes, the usage of high-voltage positive electrodes will result in a partial depletion of the lithium electrolyte layer and an increase in interfacial resistance due to the relatively lower electronegativity of sulfur compared to oxygen. When combined with lithium metal negative electrodes, it produces a larger SEI membrane impedance, causing a more serious degradation of the electrolyte-electrode interface during the cycling process. It is worth noting that sulfide organics are inorganic non-metallic particles. Furthermore, the material system exhibits high sensitivity to water and oxygen, possesses flammable properties in case of an accident, and requires the manufacturing of thin layers, all contributing to the demanding nature of the production process. Addressing this issue has consequently become imperative in the pursuit of enhancing the performance of sulfide solid-state electrolytes.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

References

- [1] Shafiee S, Topal E. When will fossil fuel reserves be diminished?. *Energy policy*, 2009, 37(1): 181-189.
- [2] Cao C, Zhong Y, Shao Z. Electrolyte Engineering for Safer Lithium-Ion Batteries: A Review. *Chinese Journal of Chemistry*, 2023, 41(9): 1119-1141.
- [3] Yang X, Adair K R, Gao X, et al. Recent advances and perspectives on thin electrolytes for high-energy-density solid-state lithium batteries. *Energy & environmental science*, 2021, 14(2): 643-671.
- [4] Wu J, Liu S, Han F, et al. Lithium/sulfide all-solid-state batteries using sulfide electrolytes. *Advanced Materials*, 2021, 33(6): 2000751.
- [5] Zhou X, Zhang Y, Shen M, et al. A highly stable Li-organic all-solid-state battery based on sulfide electrolytes. *Advanced Energy Materials*, 2022, 12(14): 2103932.
- [6] Seino Y, Ota T, Takada K, et al. A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energy & Environmental Science*, 2014, 7(2): 627-631.
- [7] Li Y, Arnold W, Thapa A, et al. Stable and flexible sulfide composite electrolyte for high-performance solid-state lithium batteries. *ACS Applied Materials & Interfaces*, 2020, 12(38): 42653-42659.
- [8] Ji W, Zhang X, Zheng D, et al. Practically Accessible All-Solid-State Batteries Enabled by Organosulfide Cathodes and Sulfide Electrolytes. *Advanced Functional Materials*, 2022, 32(27): 2202919.
- [9] Ding P, Lin Z, Guo X, et al. Polymer electrolytes and interfaces in solid-state lithium metal batteries. *Materials Today*, 2021, 51: 449-474.
- [10] Jiang P, Du G, Cao J, et al. Solid-State Li Ion Batteries with Oxide Solid Electrolytes: Progress and Perspective. *Energy Technology*, 2023, 11(3): 2201288.
- [11] Kim K J, Balaish M, Wadaguchi M, et al. Solid-state Li-metal batteries: challenges and horizons of oxide and sulfide solid electrolytes and their interfaces. *Advanced Energy Materials*, 2021, 11(1): 2002689.